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<p>(21) International Application Number: PCT/NL99/00098 (22) International Filing Date: 24 February 1999 (24.02.99) (30) Priority Data: 1010568 16 November 1998 (16.11.98) NL (71) Applicant (for all designated States except US): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): LINDEMULDER, Jan, Lodewijk [NL/NL]; Charles Voscur 33A, NL-6211 XP Maastricht (NL). BEUGELS, Jean, Hubert, Marie [NL/NL]; Brikkebekker 57, NL-6372 DV Landgraaf (NL). (74) Agent: MOOIJ, Johannes, Jacobus; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).</p>		<p>(81) Designated States: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GD, GE, HR, HU, ID, IL, IN, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report. In English translation (filed in Dutch).</p>
<p>(54) Title: POLYURETHANE COMPOSITE</p> <p>(57) Abstract</p> <p>The invention relates to a composite containing a network of parallel strong fibres, having a strength of at least 6 dN/tex, a modulus of at least 130 dN/tex and an energy absorbed during fracture of at least 8 J/g in a thermoplastic polyurethane matrix, characterised in that the matrix contains a polyurethane that is amorphous at room temperature. The invention also relates to a prepreg containing at least two layers of a network of strong fibres in a thermoplastic polyurethane matrix, the fibres and matrix being as described in the invention, and to a process for preparing the prepreg according to the invention, characterised in that strong fibres are wetted with an aqueous polyurethane dispersion and the polyurethane is amorphous at room temperature. The invention also relates to a helmet made from the composite according to the invention.</p>		

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POLYURETHANE COMPOSITE

5 The invention relates to a composite
containing a network of strong fibres, having a
strength of at least 6 dN/tex, a modulus of at least
130 dN/tex and an energy absorbed during fracture of at
least 8 J/g in a thermoplastic polyurethane matrix.
10 Such a composite is suitable for offering protection
against ballistic projectiles, in particular in
antiballistic moulded parts like helmets, panels and
vests.

 Such a composite is known from EP-A-
15 0645415. EP-A-0645415 describes a composite containing
a network of strong fibres having a tensile strength of
at least 6.18 dN/tex, a modulus of at least 132.45
dN/tex and an energy absorbed during fracture of at
least 8 J/g in a thermoplastic polyurethane matrix.

20 A drawback of such a composite is that the
impact of a projectile causes a relatively high degree
of deformation (hereafter to be called the "trauma")
behind the point of impact, as a result of which there
is a risk of a person protected by the antiballistic
25 moulded part being injured by this high degree of
deformation.

 The aim of the invention is to provide a
composite with which moulded parts can be produced
which do not show this drawback, or show it to a lesser
30 degree.

This aim is achieved according to the invention because the matrix contains a polyurethane that is amorphous at room temperature.

A "composite" is here understood to be a composition comprising at least two prepregs. Usually several prepregs are consolidated in a composite, the prepregs lying adjacent to one another preferably being at an angle of approximately 90° relative to one another.

10 A "prepreg" is understood to be a network of fibres which are held together by a matrix.

"Fibres" are here understood to be drawn objects whose length is much greater than their width and thickness. Fibres comprise continuous mono- and
15 multifilaments and also discontinuous filaments such as stacked fibres or chopped fibres.

A "network" of fibres is understood to be a composition comprising a multitude of fibres, the composition having a certain configuration. Examples of
20 configurations of the compositions are a felt, a knitted fabric and a woven fabric. Preferable is a unidirectional network in which the fibres are oriented predominantly parallel to a common fibre direction.

"Strong fibres" are in this invention
25 fibres having a strength of at least 6 dN/tex, a modulus of at least 130 dN/tex and an energy absorbed during fracture of at least 8 J/g. Strong fibres are preferably fibres having a strength of at least 10 dN/tex, a modulus of at least 200 dN/tex and an energy
30 absorbed during fracture of at least 20 J/g. More preferable are fibres having a strength of at least 16

dN/tex, a modulus of at least 400 dN/tex and an energy absorbed during fracture of at least 27 J/g. Most preferable are fibres having a strength of at least 28 dN/tex, a modulus of at least 1200 dN/tex and an energy absorbed during fracture of at least 40 J/g.

Suitable strong fibres are fibres of glass, carbon, aramide, silicon carbide and/or a drawn polymer such as drawn ultra-high-molecular polyethylene and/or combinations thereof. The fibre material preferably consists of ultra-high-molecular polyethylene.

'Ultra-high-molecular polyethylene' is understood to be polyethylene having a weight average molecular weight of at least 500,000 kg/kmol. Preferably the molecular weight is more than 2,000,000 kg/kmol.

According to the invention the fibres are incorporated in a thermoplastic polyurethane matrix which is amorphous at room temperature. Amorphous polyurethanes can be obtained via a selection obvious to a person skilled in the art of the polyols and diisocyanates of which the polyurethane is composed, as for example described in Polymer, 1991, Volume 32, pp. 343-352.

The modulus of the polyurethane can be chosen from within a wide range, depending on the requirements to be imposed on the composite with respect to the stiffness. Preferably the modulus of the polyurethane is at least 5 MPa. This will ensure that a moulded part produced from the composite according to the invention will contain no delaminations between two successive composite layers when the part has been

released from the mould after the compression at a temperature that is lower than 100°C. It has been found that moulded parts produced from a composite whose polyurethane modulus is less than 5 MPa may contain
5 delaminations between two successive composite layers after they have been released from the mould.

Preferably the matrix contains a thermoplastic polyurethane whose modulus is at least 8 MPa. This will ensure that the moulded part that has
10 been released from the mould at the temperature at which it was compressed will contain no delaminations.

The polyurethane of the matrix may contain surfactants which are used as stabilisers for a polyurethane dispersion from which the composite can be
15 produced. Preferably the concentration of surfactants in the polyurethane matrix is less than 0.01 wt.%. This will ensure that virtually no ageing of the matrix under the influence of light or heat will occur. Matrices that contain more than 0.01 wt.% of a
20 surfactant show accelerated ageing behaviour.

The invention also relates to a prepreg containing a network of strong fibres in a thermoplastic polyurethane matrix, the strong fibres and polyurethane matrix conforming to the invention.
25 Another advantage of the invention is that the prepreg contains fewer gels than when it contains a crystalline polyurethane.

Composites according to the invention could be: helmets, panels or vests. Preferably the composite
30 according to the invention is a helmet. The invention also relates to a helmet containing a first composite

according to the invention.

The stiffness of the helmet according to the invention can where necessary be increased by providing the helmet's outside surface with a layer
5 containing a second composite. Such second composites may consist of combinations of known fibres like glass, polyethylene, carbon, aramide or nylon with polymer matrices.

Preferably such a second composite consists
10 of a glass fibres in a polymer matrix. Using glass fibres ensures that the helmet can be well painted.

The polymer matrix preferably consists of a thermosetting polymer. This will ensure that the helmet whose polyurethane has a relatively low modulus can be
15 removed from the mould even at the compression temperature. Thermosetting matrices could be phenol, phenol/polyvinyl butyral, epoxy or vinyl ester.

Preferably the thermosetting matrix is a vinyl ester. This will ensure good adhesion to the
20 polyethylene fibres of the helmet.

The invention also relates to a process for the preparation of the composite according to the invention, in particular the preparation of a prepreg of which the composite is composed. Prepregs are
25 generally prepared by wetting fibres with a solution or a dispersion of a matrix material or with monomers of a matrix material in a solvent or dispersing agent. The fibres can also be wetted with a melt of the matrix material. The wetted fibres are usually applied to a
30 support, after which the solvent or dispersing agent is removed from them on a drying line, if necessary, in an

oven and they are subsequently cooled. Such a process is known from EP-A-0645415. In EP-A-0645415 strong polyethylene fibres are wetted with an aqueous solution in which an aliphatic diisocyanate monomer and a polyol
5 monomer have been dispersed. During the evaporation of the water the monomers polymerise to form the polyurethane.

A drawback of such a process is that the polymerisation and evaporation take a relatively long
10 time. EP-A-0645415 describes that a drying line with a length of 10 m is required for this purpose.

The aim of the invention is to provide a process with which a substantially shorter drying line suffices.

15 This aim is achieved according to the invention because strong fibres are wetted with an aqueous polyurethane dispersion and the polyurethane is amorphous at room temperature.

It has surprisingly been found that when
20 use was made of an aqueous dispersion of a polyurethane that is amorphous at room temperature, a drying line of only two metres sufficed at a production rate of approx. 15 m/min. Another advantage of the process according to the invention is that the prepreg produced
25 according to this process contains no, or virtually no gels. When the fibres are wetted with the solution of monomers known from EP-A-0645415 it was not possible to produce a prepreg in a drying line with a length of 2 m at an economically somewhat acceptable production rate
30 and the prepreg produced in the known manner contained a large number of gels. A 'gel' is understood to be a

local thickening of the matrix material on the prepreg. Such thickenings lead to undesired irregularities in the prepreg and the composite produced from it.

The composite according to the invention is
5 produced by stacking two or more prepregs, with the angle between the fibres of two prepregs lying adjacent to one another being substantially larger than 0° . Preferably the angle between two prepregs lying adjacent to one another is approximately 90° . The stack
10 of prepregs is subsequently consolidated by compressing it at elevated temperature. Composites containing two or four prepregs can be stacked and processed into a flexible object such as an anti-ballistic vest. In that case no specific demands are imposed on the modulus of
15 the polyurethane.

It is also possible to form a hard object from the prepregs by compressing several layers to form a composite in a mould. The compression is generally effected at a temperature of between 100 and 130°C . If
20 a hard object is compressed, the polyurethane preferably has a modulus of at least 5 MPa . This will ensure that the composite can be released from the mould at a temperature of at least 100°C without any delamination taking place during the release from the
25 mould. This presents the advantage that the mould does not have to be cooled to below 100°C to release the moulded part from the mould, and subsequently heated again for the compression of the next moulded part.

The modulus is here understood to be the
30 secant modulus measured in a film of the polyurethane at 100% elongation.

Preferably the polyurethane has a modulus of at least 8 MPa. This will ensure that the moulded part can be released from the mould at the compression temperature, so that the mould need not be cooled at all, which is very advantageous from both an energetic and an economic viewpoint. A condition is that the polyurethane and the matrix adhere well to one another. This is ensured by the characteristics of the process according to the invention.

As the mass of the mould with which a helmet is produced is relatively large owing to the voluminous core, relatively large amounts of time and energy are required to heat and cool such a mould for each moulded part. The advantages of the characteristics of the invention are hence particularly evident in the production of a helmet. As a consequence, relatively little energy is required to produce a helmet according to the invention and the cycle time in compression is relatively short.

Surfactants are often used in the production of polyurethane dispersions to stabilise the dispersion. In the process of the invention use is preferably made of a polyurethane dispersion containing less than 0.01 wt.% of a surfactant. This will ensure that the drying can proceed even faster and that no bubbles are formed between the support and the formed prepreg during the drying.

The invention will be further elucidated with reference to the examples without restricting itself hereto.

The 'trauma' effect is determined and

characterised with the bulging of the object behind the point of impact of a projectile. The trauma was measured according to standard EN ISO 14876-3. The plastiline employed is Caran D'ache type "Modella Essai, CDA 259.001". The standard prescribes that the
5 plastiline be heated to a temperature at which a bullet with a diameter of 63.5 mm and a weight of 1043 grams results in an impression with a depth of 20 ± 2 mm at a falling height of 200 cm. In the comparative tests
10 described hereafter the plastiline was used at a constant temperature of 20 ± 2 °C. At this temperature the impression caused by said bullet fallen from a height of 200 cm is 17-19 mm.

15 Examples

Example I

A network of 52 g/m² unidirectionally oriented Dyneema SK76 yarn with a modulus of 1180
20 cN/dTex, a strength of 36 cN/dTex and a titre of 1760 dTex was impregnated with an aqueous dispersion of "Witcoflex 130 Matt" polyurethane (Baxenden Chemicals, 100% Tensile modulus = 5 MPa). The aqueous dispersion contains 28% solids. The impregnated web was dried on a
25 drying bridge with a length of 2 metres at a temperature of 100-103°C at a transport speed of 6 m/min. At higher transport speeds the residual volatiles content rises above 1%. The prepreg thus obtained has an areal density of 70 gr/m² and contains
30 25.7% matrix. Via 0/90/0/90° stacking of 4 layers of impregnated prepreg a laminate of 280 g/m² is produced

with a calender. A number of the laminates thus produced were compressed for 30 minutes at 10 bar and 128°C to form a composite panel. The compressed panels were released from the mould at 100°C and were

5 ballistically tested against different threats. The results of these tests are given in Table 1a.

Table 1a:

Ballistic evaluation of UD laminate based on Witcoflex

10 130 PUR matrix.

Threat	Number of laminates	Areal density [kg/m ²]	V50 [m/s]	Amount of energy absorbed [J/kg/m ²]
17 grain FSP	25	7.0	617	29.8
9 mm parabellum	10	2.8	388	216
.357 GECO	18	5.2	474	222
7.62x51 NB	75	21.2	833	155

Next, 10-layer compressed composites based on UD with

15 Witcoflex 130 Matt (25.7% matrix) were fired at with 5 9-mm parabellum bullets with a speed of ± 340 m/s and with 5 7.62 Nato Ball bullets with a speed of ± 800 m/s on a plastiline backing (Caran d'Ache). The bullets' speed and the trauma they caused were measured and the

20 average is presented in Table 1b.

Comparative Experiment 1

10-layer compressed panels based on UD with Dispercoll U42 polyurethane (24.8% matrix) were produced in the same way as in Example I and they were fired at in the same way as described above. The results of this are given in Table 1b. Dispercoll U42 is a semi-crystalline matrix.

10 Table 1b:

Trauma of UD-Witcomatt 130 versus UD-Dispercoll U42 measurements

Threat	Matrix	Number of layers	areal density [kg/m ²]	V [m/s]	Trauma [mm]
9 mm parabellum	Witcomatt 130	10	2.8	341	22
9 mm parabellum	Dispercoll U42	10	2.8	339	27
7.62 nato ball	Witcomatt 130	75	21.2	794	28
7.62 nato ball	Dispercoll U42	75	21.1	796	34

This shows that a polyurethane matrix based on a polyurethane that is amorphous at room temperature results in a lesser trauma than a polyurethane based on a semi-crystalline polyurethane.

Example II

The network was impregnated according to Example I, except that Witcobond 736 (Baxenden Chemicals, 100% modulus = 8 MPa) was used as the aqueous polyurethane dispersion. Witcobond 736 has a solids content of 40%. The transport speed of the impregnated web on the drying line is 15 m/min, the residual volatiles content of the prepreg obtained being lower than 1%. The prepreg has an areal density of 68 g/m² and contains 22.4% matrix. Via 0/90/0/90° stacking of 4 layers of prepreg a laminate of 272 g/m² was produced with the aid of a calender. 10 layers of the laminate obtained were compressed for 30 minutes at 10 bar and 128°C to form a composite panel. The panels were released from the mould at 100°C. The compressed panels were ballistically tested against different threats.

The results are presented in Table 2.

Table 2:

Ballistic evaluation of UD laminate based on Witcobond 736 PUR matrix.

Threat	Number of layers	Areal density [kg/m ²]	V50 [m/s]	Amount of energy absorbed [J/kg/m ²]
9 mm parabellum	10	2.7	396	234
.357 GECO	18	5.2	465	225

At an average speed of 340 m/s, 9-mm parabellum bullets result in a trauma of 21 mm.

Example III

5 The network was impregnated according to
Example I, except that Witcobond 246-41 (Baxenden
Chemicals, 100% Tensile modulus = 6 MPa) was used as
the polyurethane dispersion. Witcobond 246-41 has a
10 impregnated network on the drying bridge is 15 m/min,
the residual volatiles content of the prepreg being
lower than 1%. The prepreg obtained has an areal
density of 65 g/m² and hence contains 20% matrix. Via
0/90/0/90° stacking of 4 layers of prepreg a laminate
15 of 260 g/m² was produced with the aid of a calender.
The laminate obtained was compressed for 30 minutes at
10 bar and 128°C to form a composite panel. The panels
were released from the mould at 100°C. The compressed
panels were ballistically tested against 9-mm
20 parabellum bullets. The results are presented in Table
3.

Table 3:

Ballistic evaluation of UD laminate based on Witcobond 246-41 PUR matrix.

Threat	Number of layers	areal density [kg/m ²]	V50 [m/s]	Amount of energy absorbed [J/kg/m ²]
9 mm parabellum	10	2.7	419	269

5

At an average speed of 337 m/s, 9-mm parabellum bullets result in a trauma of 22 mm.

Example IV

10 18 layers of laminate of Example II were compressed to form a composite panel according to Example II, except that the panel was compressed for 10 minutes at 128°C, and the mould was opened at this temperature. The ballistic performance against .357

15 GECO was determined. The performance is the same as that of a panel cooled to 100°C before being released from the mould. Releasing the compressed panels based on UD\Witcobond 736 from the mould while hot results in no delamination and a stiffness and ballistic

20 performance comparable with those of panels that were cooled to 100°C before being released from the mould. The ballistic performance of these plates is presented in Table 4.

Table 4:

Releasing UD laminate based on Witcoflex 736 PUR matrix from the mould while hot.

Threat	Number of layers	Areal density [kg/m ²]	V50 [m/s]	Amount of energy absorbed [J/kg/m ²]
.357 GECO	18	5.2	462	224

5

Example V

The UD laminate of Example II was used to compress helmets. 22 squares of 45 x 45 cm UD laminate were used to deep-draw the helmet. 5 circles (diameter 30 cm) of UD laminate were added at the crown of the helmet. The helmets were compressed for 20 minutes at 128°C and a pressure of 225 tonnes, after which the mould was opened. The helmet's weight is 907 grams. The helmet showed no delaminations. The helmet's ballistic performance was tested against 17 grain FSP according to Stanag 2920. The V50 is 677 m/s.

Example VI

Example V was repeated, except that the helmet was finished by adding 1 layer of glass\vinyl ester to the helmet's inside and outside surfaces. The employed glass\vinyl ester has an areal density of 270 g/m² and a vinyl ester content of 50%. The helmet of Example VI has a smoother surface and a greater stiffness than the helmet of Example V and can moreover

be painted better. The UD laminate and glass\vinyl ester woven fabric adhere well to one another; no delaminations were visible. Surprisingly, the glass/vinyl ester composite has no negative effect on
5 the V50 against 17 grain FSP.

Example VII

Example VI was repeated, except that aramide woven fabric\vinyl ester was used instead of
10 glass\vinyl ester. The aramide woven fabric\vinyl ester employed has an areal density of 285 g/m² and a vinyl ester content of 20%. The helmet of Example VII has a smoother surface and a greater stiffness than the helmet of Example V and can moreover be painted well.
15 The helmet of Example VII has a lower stiffness than the helmet of Example VI and the paint adheres less well than the helmet of Example VI. The addition of the aramide\vinyl ester woven fabric employed has virtually no positive influence on the V50 against 17 grain FSP.

C L A I M S

1. Composite containing a network of parallel strong
5 fibres, having a strength of at least 6 dN/tex
and a modulus of at least 130 dN/tex and an
energy absorbed during fracture of at least 8 J/g
in a thermoplastic polyurethane matrix,
characterised in that the matrix contains a
10 polyurethane that is amorphous at room
temperature.
2. Composite according to Claim 1, characterised in
that the modulus of the polyurethane is at least
5 MPa.
- 15 3. Composite according to Claim 1 or Claim 2,
characterised in that the modulus of the
polyurethane is at least 8 MPa.
4. Composite according to any one of Claims 1-3,
characterised in that the composite contains less
20 than 0.1 wt.% of a surfactant.
5. Prepreg containing at least two layers of a
network of strong fibres in a thermoplastic
polyurethane matrix, with the fibres and matrix
as described in any one of Claims 1-4.
- 25 6. Helmet containing a first composite according to
any one of Claims 1-4.
7. Helmet according to Claim 6, the outside surface
of the helmet being provided with a second
composite containing glass fibres in a
30 thermosetting matrix.
8. Helmet according to Claim 7, the thermosetting

matrix being a vinyl ester.

9. Process for the preparation of a prepreg according to Claim 5, characterised in that strong fibres are wetted with an aqueous polyurethane dispersion and the polyurethane is amorphous at room temperature.
10. Process according to Claim 9, characterised in that the modulus of the polyurethane is at least 5 MPa.
- 10 11. Process according to Claim 9 or Claim 10, characterised in that the composite contains less than 0.1 wt.% of a surfactant.
12. Use of the prepreg according to Claim 5 for the production of a helmet.

INTERNATIONAL SEARCH REPORT

In tional Application No
PCT/NL 99/00098

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08J5/04 F41H5/04 //C08L75:04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08J F41H B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 645 415 A (ALLIED SIGNAL INC) 29 March 1995 (1995-03-29) cited in the application claims 1,6-8 ---	1,5,6,9, 12
Y	US 4 983 433 A (SHIRASAKI YOSHIKAZU) 8 January 1991 (1991-01-08) claims 1,3 column 4, line 10 - line 40 ---	1,5,6,9, 12
A	WO 91 08895 A (ALLIED SIGNAL INC) 27 June 1991 (1991-06-27) abstract; claims 1,6,8-10 --- -/-	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	STEINBERGER R: "GLASFASERVERSTAERKTE THERMOPLASTISCHE POLYURETHANE. REINFORCING THERMOPLASTIC POLYURETHANES WITH GLASS FIBRES" KUNSTSTOFFE, vol. 82, no. 12, 1 December 1992 (1992-12-01), pages 1181-1182, 1183 -, XP000330339 ISSN: 0023-5563 the whole document ----	1
A	EP 0 585 793 A (ALLIED SIGNAL INC) 9 March 1994 (1994-03-09) claims 1,2,8 page 6, line 24 - line 49 ----	1
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INTERNATIONAL SEARCH REPORT

Information on patent family members

In: International Application No

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